Determination of trap distribution of nanocomposites based on the voltage response measurement

INNOVATION OF POLYMER NANOCOMPOSITE MATERIALS FOR ELECTRICAL ENGINEERING

Zoltán Ádám Tamus

Budapest University of Technology and Economics, Hungary

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Objectives of the Research

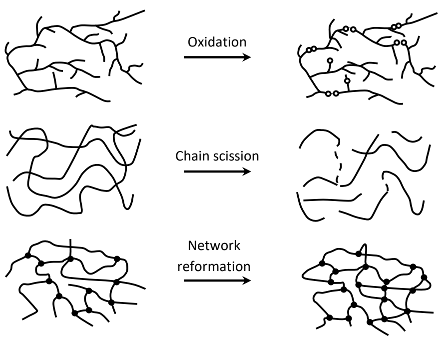
- Investigating the nanocomposite dielectrics degradation processes in case of extreme environment.
- Identifying the degradation processes of potential dielectric nanocomposites.

- The knowledge of degradation processes enables to develop a dielectric measurement based non-destructive technique, which capable to track the degradation of nanocomposite dielectrics.

- Background:
  - Nanoparticles can improve the radiation resistance of the polymer matrix
  - Addition of nanoparticles can mitigate free radicals generated by radiolysis
  - Several investigations lead on possible application of superconducting magnets

Theoretical Background of Non-destructive Material Testing

- Chain scission
- Cross linking
- Evaporation of by products
- Oxidation



- Extreme temperature
- Pressure
- Radiation
- Chemical spraying

Stresses in operation

Material structure

***C*:** concentration of a component, which determines the properties

$P_c = f_c(C)$

$P_d = f_d(C)$

Critical properties (P_c)

measured by destructive method
e.g. breakdown voltage, EAB, chemical tests

Diagnostic properties (P_d)

measured by non-destructive method
e.g. indenter, electrical tests, hardness

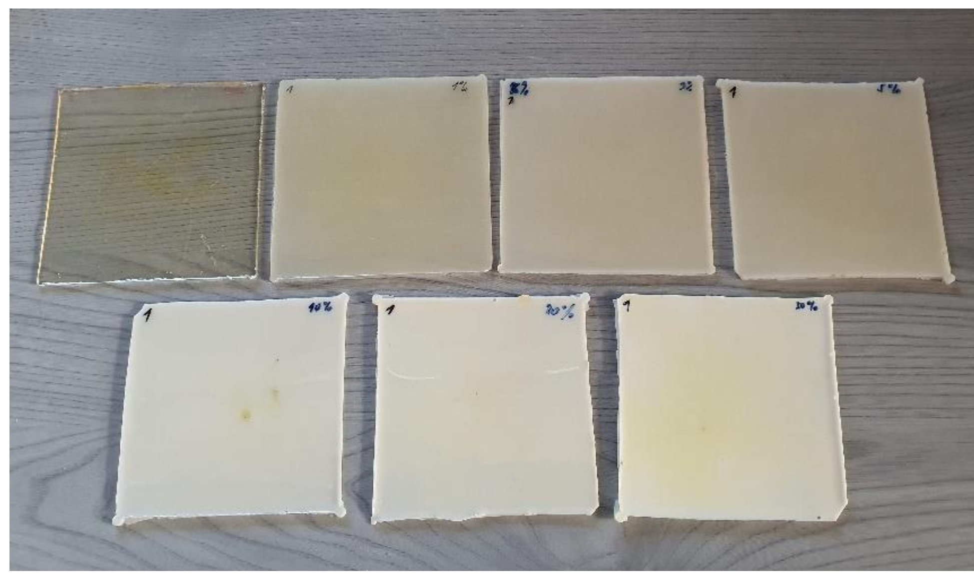
TAMUS, Z. A., et al. Insulation Diagnostics of High Voltage Equipment by Dielectric Measurements-Hungarian Research and Experience. In: 2016 Int. Scientific Symposium-Electrical Power Engineering. 2016. p. 7-13.

STANDARD MEASURMENTDS ON EPOXY NANOCOMPOSITES

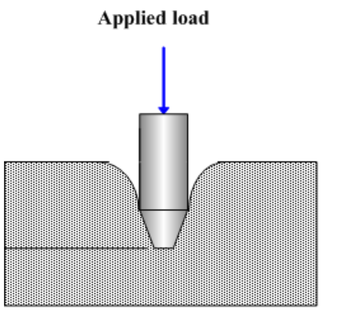
Sample preparation

- Matrix material: epoxy resin ELAN-TECH EC 141 on the base of Bisphenol-A Epichlorohydrin
- Filling material: magnesium oxide (MgO) nanoparticles
  - wide bandgap (7.5 eV)
  - high volume resistivity (10^{17} Ωcm)
- 100x100 mm samples
- thickness: 1…2 mm
- nanoparticle content (wt%):
  - Pure
  - 1%, 3%, 5%, 10%, 20% and 30%.

Parameter	Value
Glass transition temperature	58°C
Max operation temp.	130°C
Tensile strength	47 MN/m^2
Flexural elastic modulus	2700 MN/m^2
Flexural strength	78 MN/m^2



Measurement methods I. – Shore D hardness



Shore D:

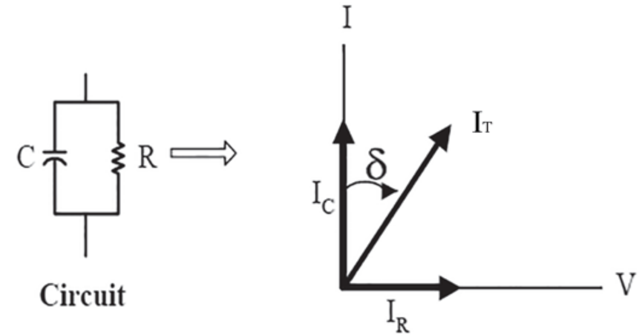
- 44.45 N applied force
- Indenter foot: 30° cone, 1.40 mm
- Hardness: 0 (soft)..100 (hard)
- Indention depth: 2.54 mm
- Hardness: 0 (soft)..100 (hard), (indention: 2.54…0 mm)
- Measurement time: 3 s

- Number of measurements: 10 points on each sampe (highes and lowest values were rejected)
- Temperature: 26.5°C

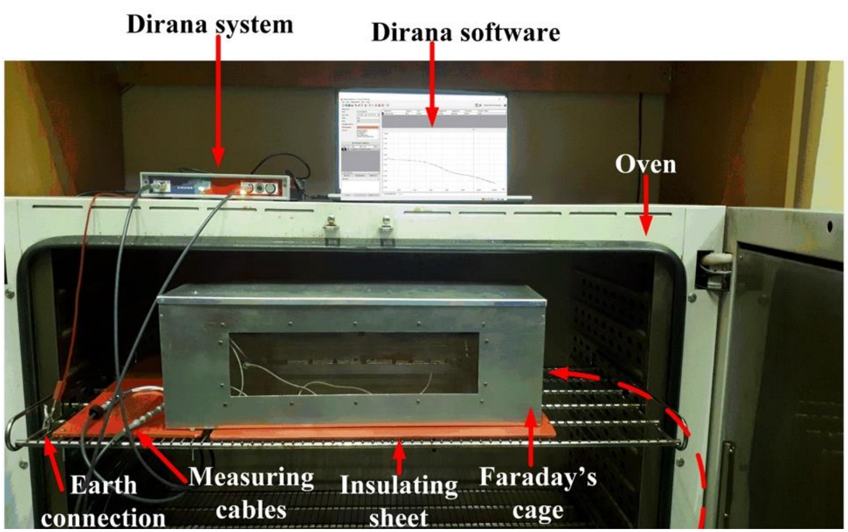
Measurement methods II. – loss factor (tan delta)

Dissipation factor:

- **Omicron Dirana**:
  - Combination of frequency-domain spectroscopy (FDS) and polarization-depolarization current (PDC) methods to determine the dielectric response
  - Shorter measurement time

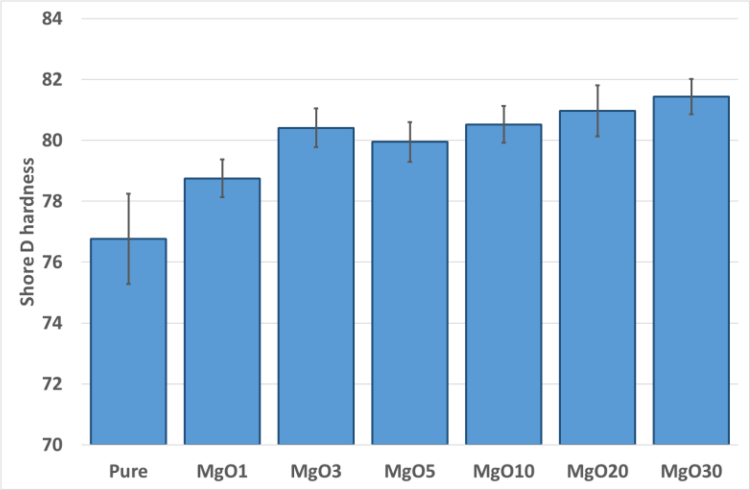


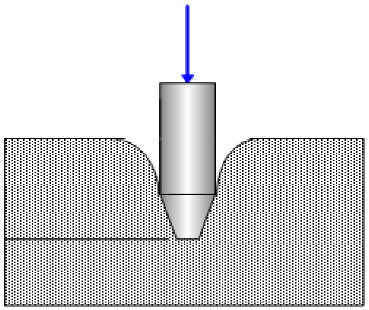
- Frequency range is 300 µHz…1 kHz
- The test voltage was 100 V_{rms} in FDS mode and 200 V_{dc} in PDC mode.
- The FDS method was used between 0.1 Hz and 1 kHz. The PDC method was used below 0.1 Hz.



Tasks executed on epoxy resin samples I.

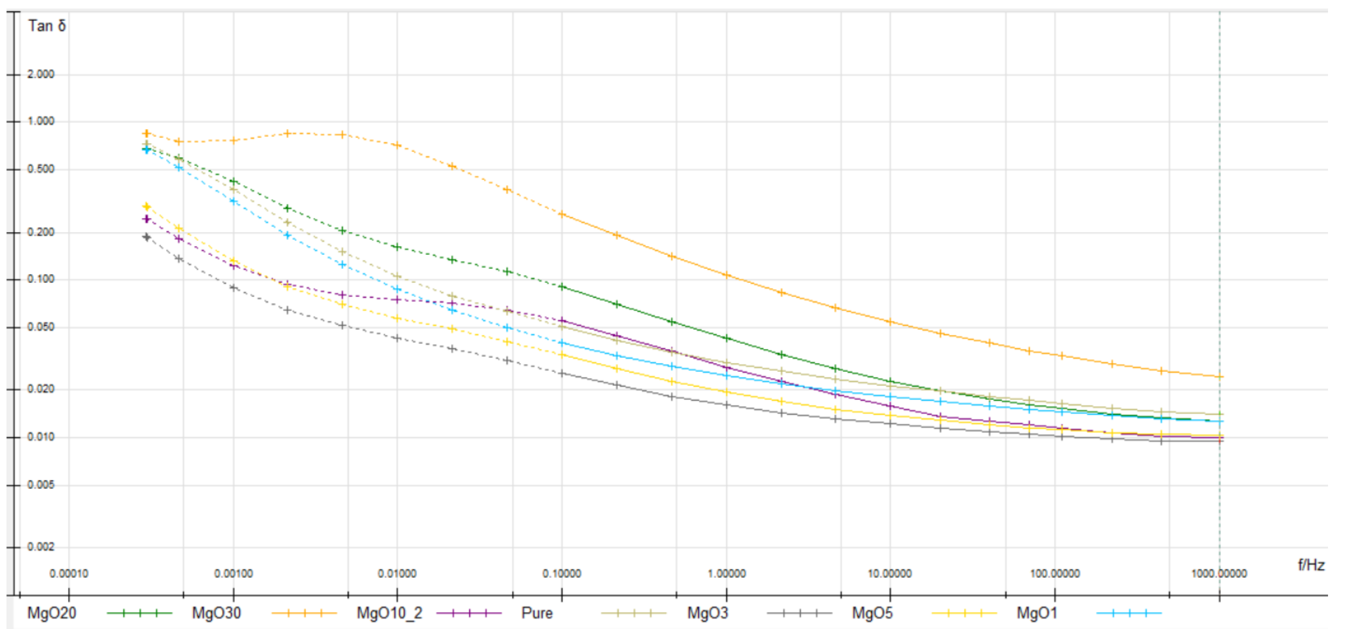
- The epoxy resin samples were prepared and characterized by non destructive methods
  - Shore D hardness
  - Dielectric measurements in low frequency range. Temperature dependence investigated.
- The hardness values increase with MgO content but 5wt% shows local minimum.





Tasks executed on epoxy resin samples II.

- Dielectric spectroscopy data suggest the lowest DF has 3wt% sample at low frequency, but around 1 kHz the trend is not clear.
  - Measurement at higher frequencies (100 kHz MHz range) to reveal other polarization processes
- Positive temperature dependence -> shallow traps – space charge polarization



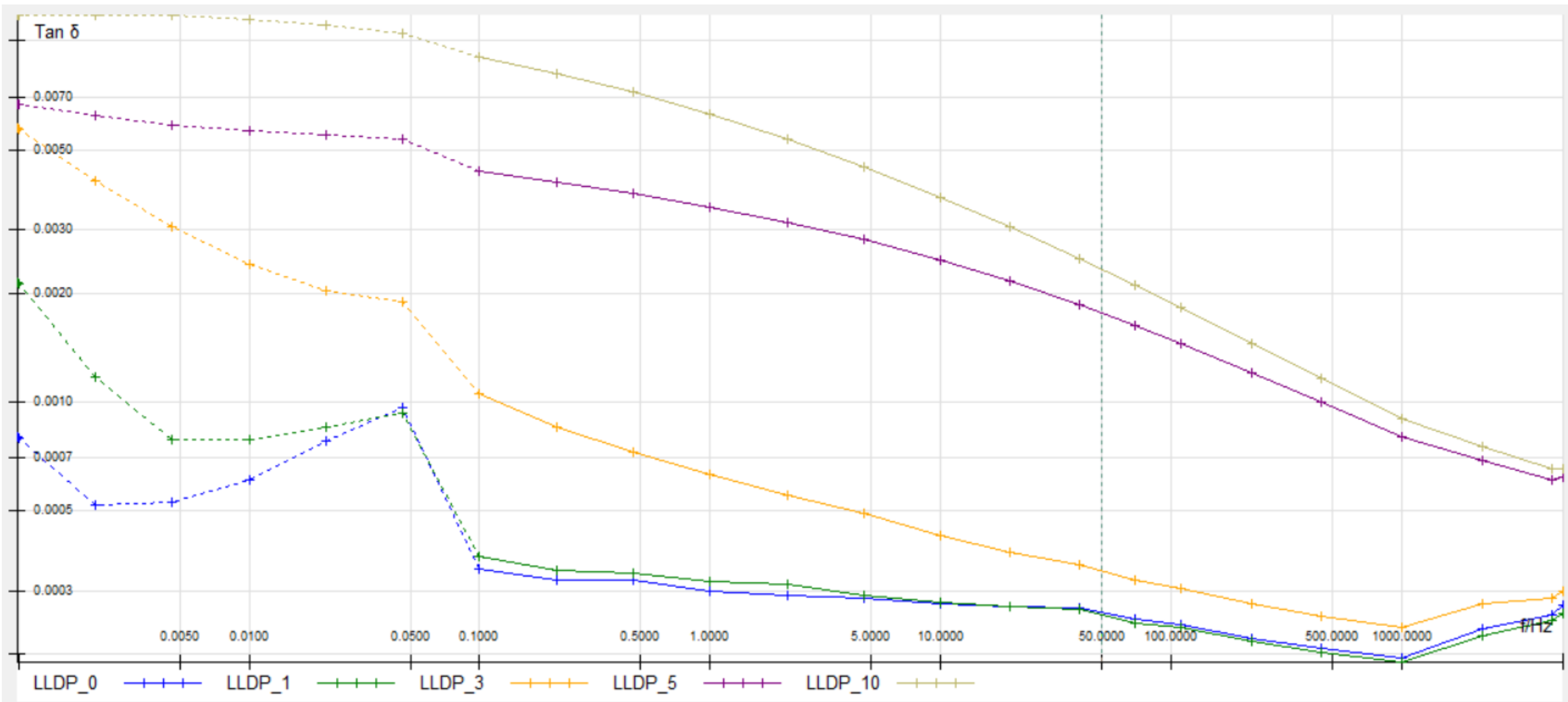
STANDARD MEASURMENTDS ON LLDPE NANOCOMPOSITES

Sample Preparation - LLDPE

- MgO was dispersed in the polymer matrix melt at 180 °C and a screw speed of 60 rpm.
- The extruded strings were granulated after cooling in air.
- The film was extruded from the obtained granulated material .
- The temperature profile along the screw towards the extrusion head was set at 180-180-180-185 °C (four heating zones),and the screw speed was set at 50 rpm.
- The film was removed immediately downstream of the extrusion head
- Thickness: app. 0.2 mm

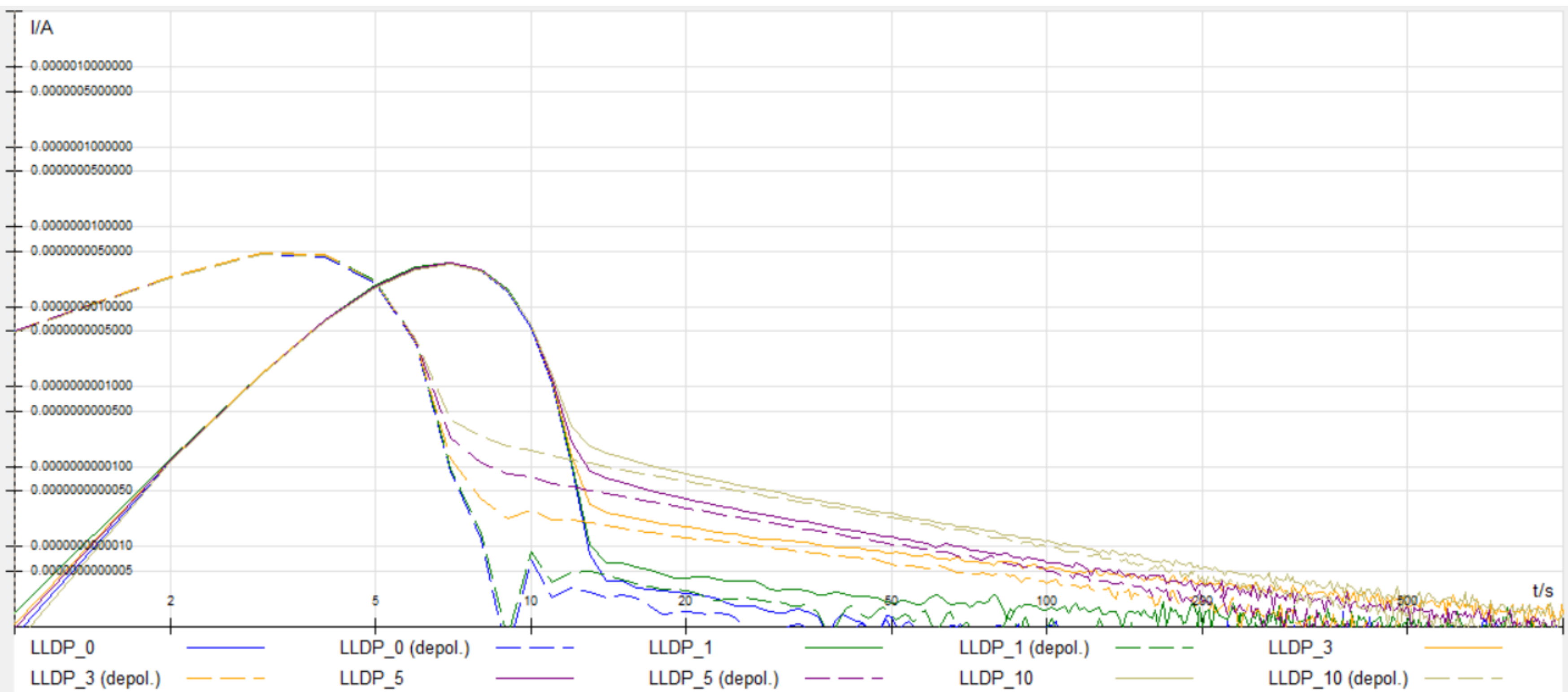
LLDPE — Tan delta @ 25°C

- The tan delta values are quite low, close to the measurable limit
- PDC method was not able to measure the samples



LLDPE samples — the PDC curves

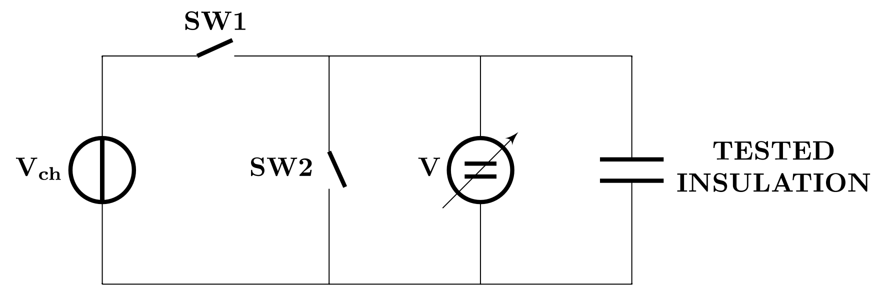
- Problem: too low currents, lower than the current (around 70 fA)



DETERMINATION OF TRAP DISTRIBUTION BASED ON EVR

Extended voltage response method

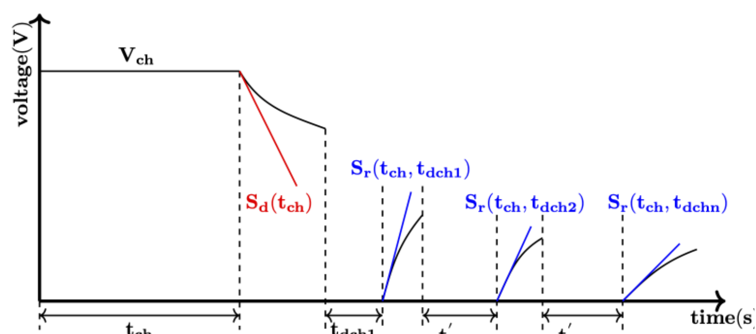
- The **extended voltage response** measurement is based on the **measurement of decay and return voltages**.
- The decay voltage can be measured after a long charging time (t_{ch}) of the cable insulation disconnecting the voltage source
- The slopes of return voltages ($S_r(t_{dch1})$… $S_r(t_{dchn})$) can be measured on the charged insulation after different shorting times (t_{dch1}…t_{dchn})



- The relationship between the results and the dielectric characteristics can be expressed:

$$S_d = \frac{V_{ch}}{dt}\Big|_{t=t_{ch}} = -\frac{i_{pol}(t_{ch})}{C} = -\frac{V_{ch}}{\varepsilon_1}\left[\frac{\sigma_0}{\varepsilon_0} + f(t_{ch})\right]$$

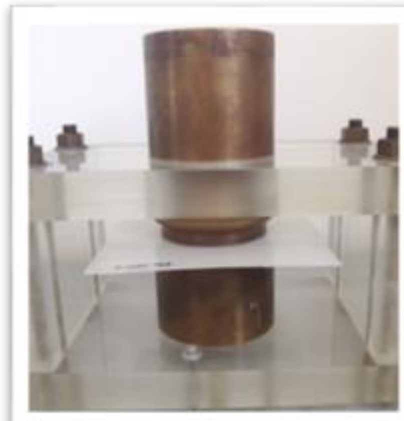
$$S_r = \frac{V_{ch}}{\varepsilon_\infty}\left[f(t_{dch}) - f(t_{dch} + t_{ch})\right]$$



Tamus Z Á, Csábi D and Csányi G M 2015 Journal of Physics: Conference Series 646 012043

The electrode arrangement and conditions

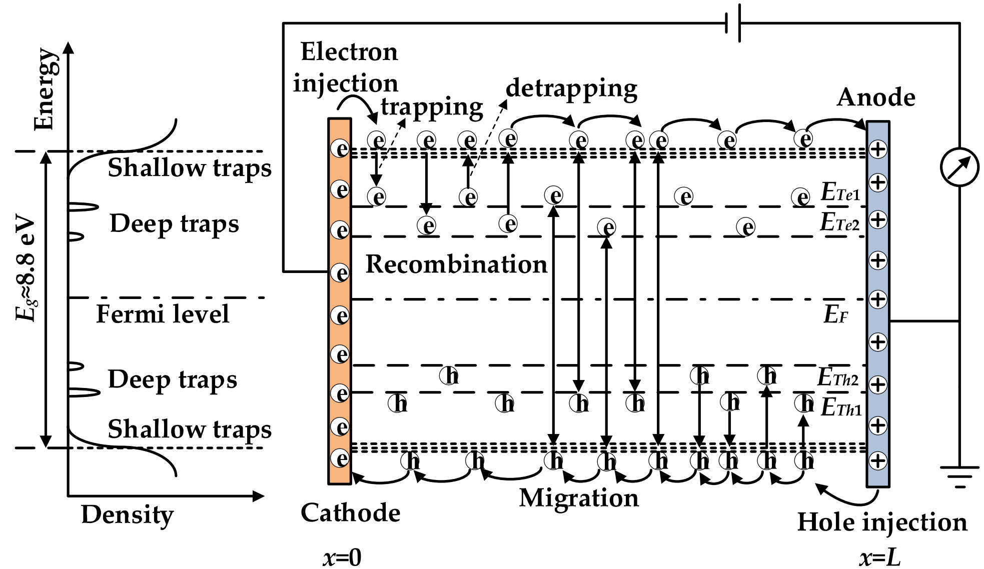
- The two electrodes were copper cylinders with 35.6 mm diameter.
- The relative humidity and temperature was monitored during the measurements.
- Epoxy resin samples
  - Room temperature (22°C)
  - 40°C
  - 50°C
- LLDPE at room temperature (25 °C)



The isothermal relaxation current

- The degradation of polymers affects the dielectric properties such as conduction and polarization.
- The slow polarization processes are related to the electron trapping and de-trapping mechanisms.
- The de-trapping of electrons in a charged polymer leads to an isothermal relaxation current (IRC).

- The residence time of carriers:
- 10^{-13} s for a level at 0.1 eV
- 500 s for a level at 1 eV



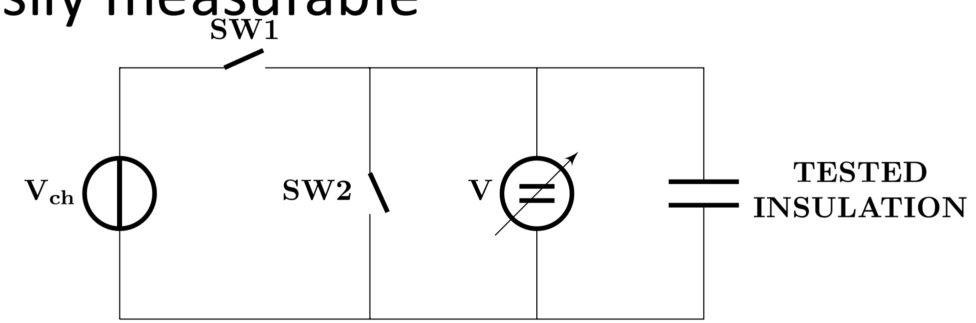
Xing, Z.; Zhang, C.; Cui, H.; Hai, Y.; Wu, Q.; Min, D. Space Charge Accumulation and Decay in Dielectric Materials with Dual Discrete Traps. *Appl. Sci.* **2019**, *9*, 4253. https://doi.org/10.3390/app9204253

Calculation of trap distribution

- According to the theory of Simmons and Tam, this current function can be expressed as:

$$j(t) = \frac{eLk_BT}{2t} f_0(E)N(E)$$

- where *e* is the electron's charge, *L* is the thickness of the insulation k_B the is the Bolzmann's constant, *T* is the absolute temperature, $f_0(E)$ is the initial distribution of traps, *N(E)* is the trap density.
- The IRC charging the capacitance of the test object and the measurnig equipment — easily measurable



J. G. Simmons and M. C. Tam, "Theory of isothermal currents and the direct determination of trap parameters in semiconductors and insulators containing arbitrary trap distributions," Physical Review B, vol. 7, pp. 3706–3713, 04 1973.

Calculation of trap distribution based on EVR results — I.

- Hence the slope of return voltage proportional to the trap distribution:

$$N(E) = \frac{2tj(t)}{eLk_B T f_0(E)} = \frac{2t_{dch} S_r(t_{dch}) C}{eLk_B T f_0(E) A} = \frac{2t_{dch} S_r(t_{dch}) C}{ek_B T f_0(E) v}$$

- As deducted, the trap depth is related to time, now the discharging time:

$$E_t = k_B T \ln t_{dch}$$

Calculation of trap distribution based on EVR results — II.

- Assuming two, shallow and deep traps, the slope of return voltage is approximated as a sum of two exponentials (two Debye processes):

$$S_r(t_{dch}) = A_1 e^{-t_{dch}/\tau_1} + A_2 e^{-t_{dch}/\tau_2}$$

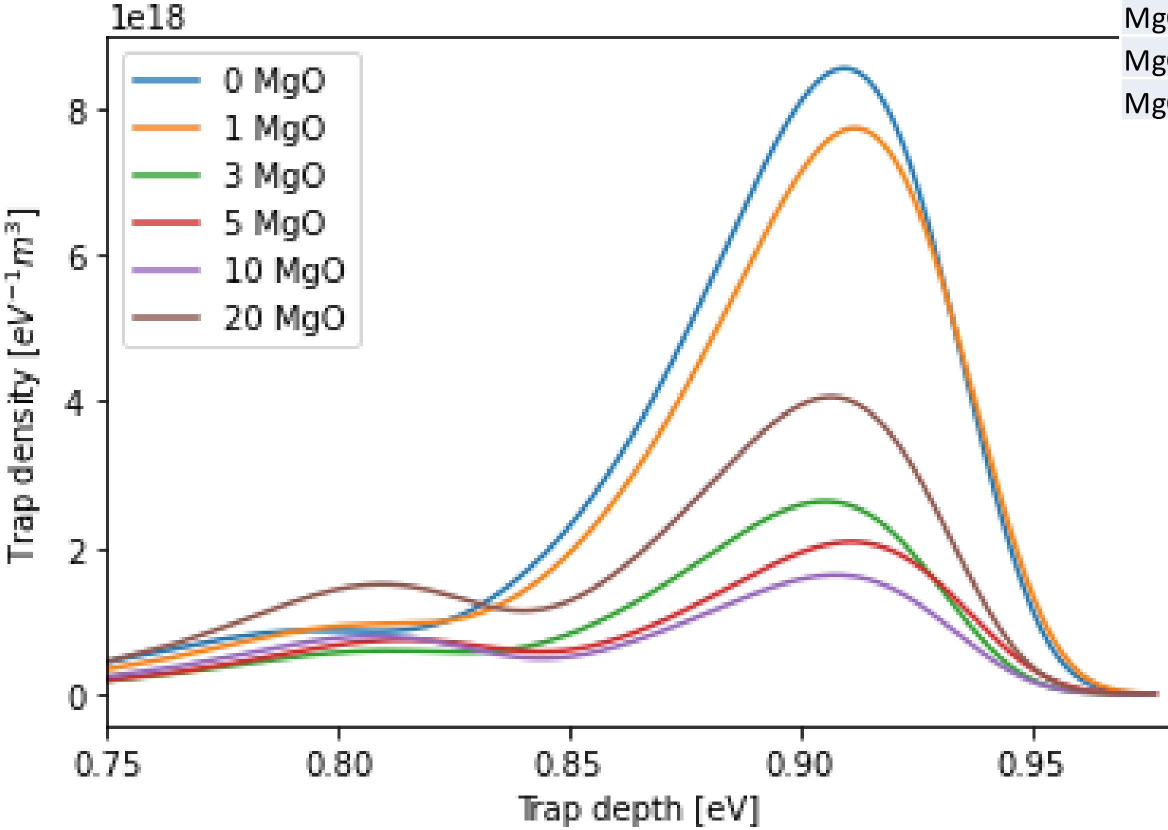
- The EVR provides the set of $S_r(t_{dch})$ values, using Python's SciPy optimization library, the A_1, A_2, τ_1 and τ_2 values are estimated.
- Plotting *N(E)* vs. $k_B T \ln(vT)$

CALCULATED TRAP DISTRIBUTION OF NANOCOMPOSITES

Results — epoxy resin samples I.

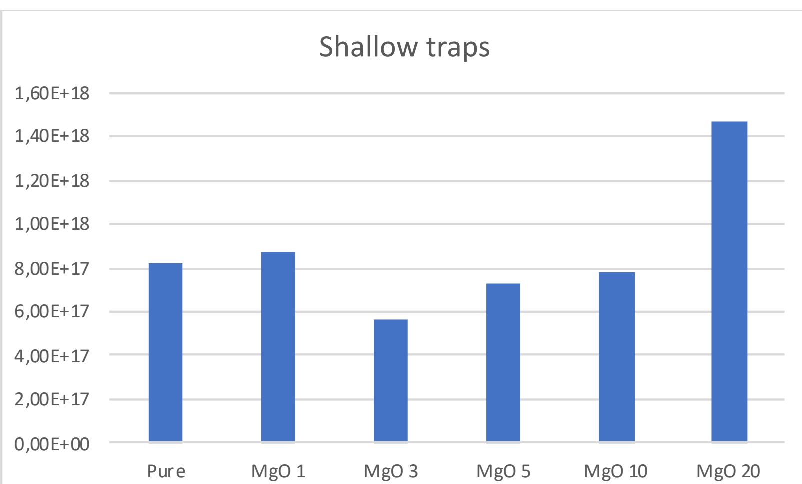
- Two traps identified:
  - Shallow at 0.79 eV
  - Deep at 0.91 eV

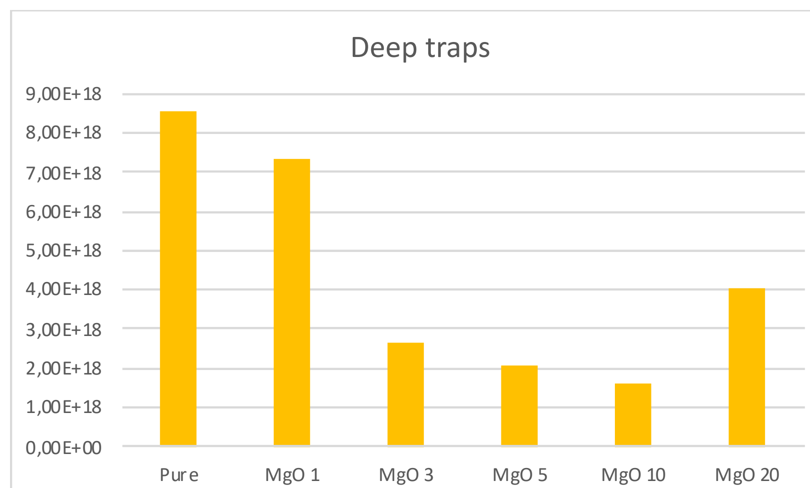
	shallow		deep	
	eV	eV-1m-3	eV	eV-1m-3
Pure	0,78	8,21E+17	0,91	8,55E+18
MgO 1	0,79	8,75E+17	0,91	7,33E+18
MgO 3	0,8	5,65E+17	0,91	2,63E+18
MgO 5	0,81	7,27E+17	0,91	2,07E+18
MgO 10	0,8	7,85E+17	0,91	1,62E+18
MgO 20	0,8	1,47E+18	0,91	4,06E+18



Results – epoxy resin II.

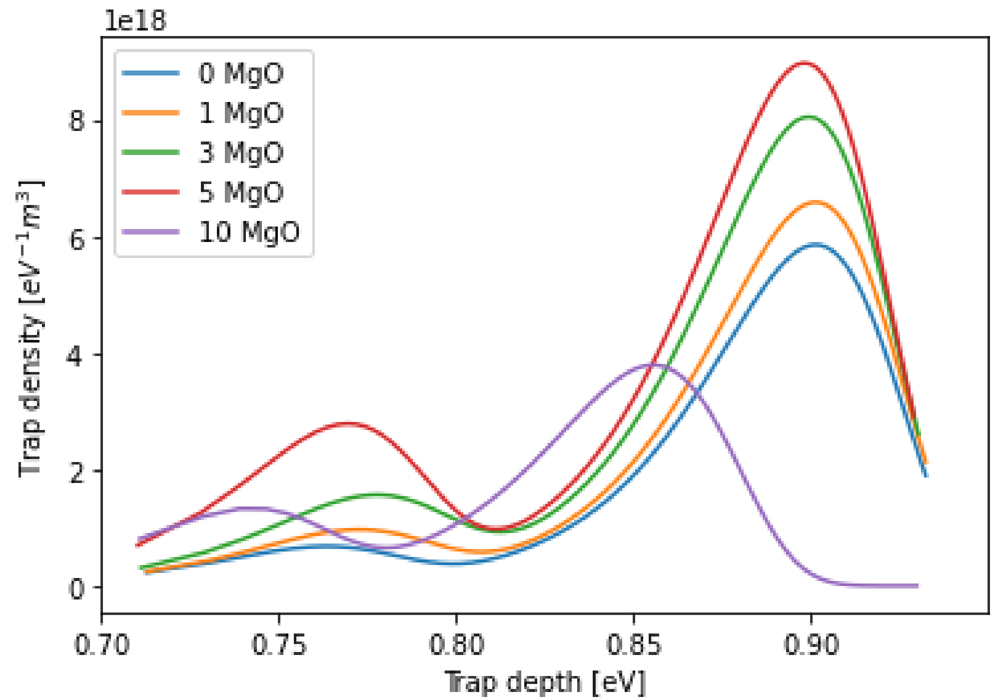
- The MgO 3 samples has lowest shallow trap density
- While lowest deep trap density has the MgO 10



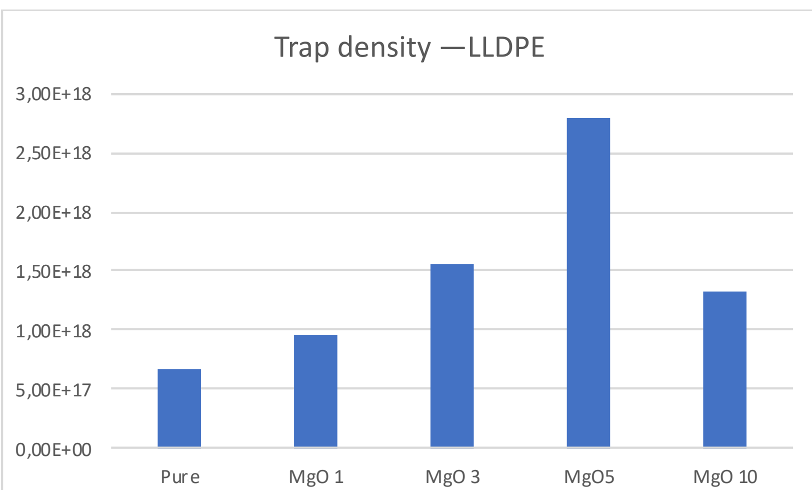


Results — LLDPE

- Deep traps are not valid, the maximum t_{dch} was 300 s !
- Hence the maximum $\boldsymbol{\tau}$ is 1500 s



	eV	eV-1m-3
Pure	0,76	6,73E+17
MgO 1	0,77	9,60E+17
MgO 3	0,77	1,55E+18
MgO5	0,77	2,79E+18
MgO 10	0,74	1,33E+18

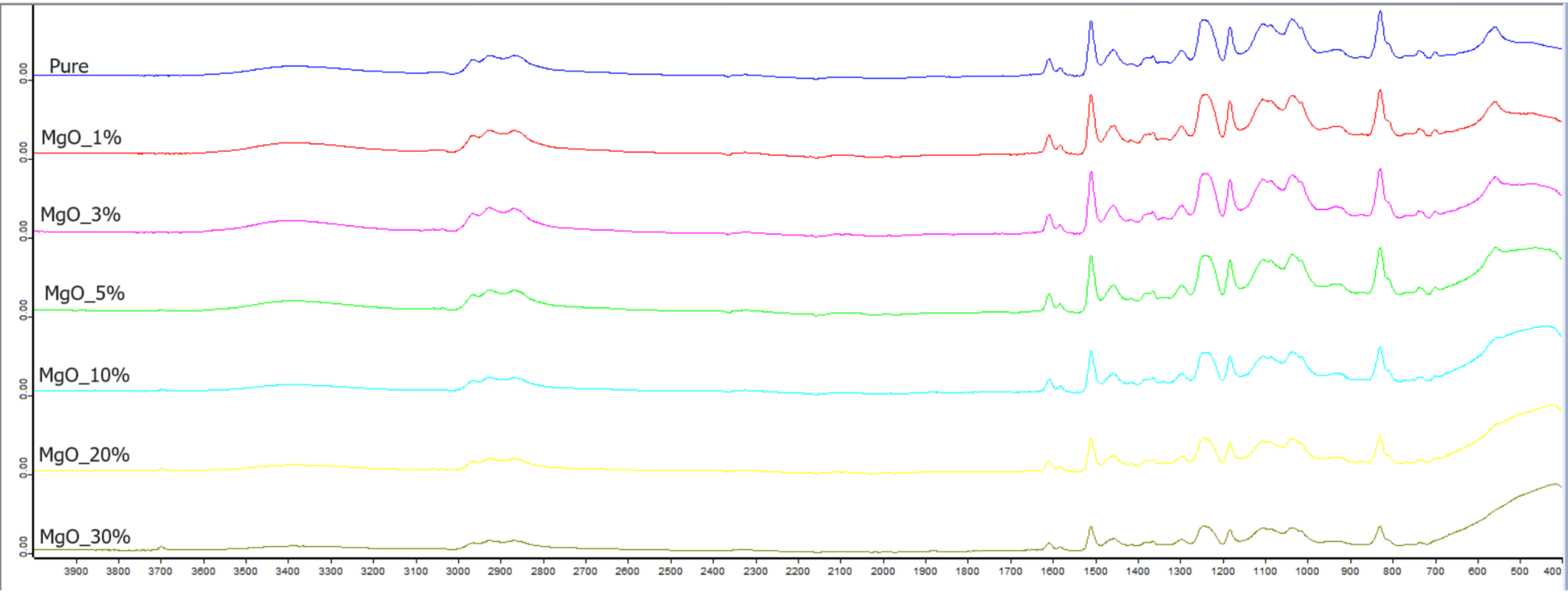


FTIR analysis

- MgO absorbance regions according to the literature:
  - Mg-O-Mg resonance:
    - 600-850 cm^{-1}
    - 487-677 cm^{-1}
    - 473 cm^{-1}
  - surface hydroxil group: 1434 cm^{-1}
  - OH:
    - 3702 cm^{-1}
    - 3300-3600 cm^{-1}

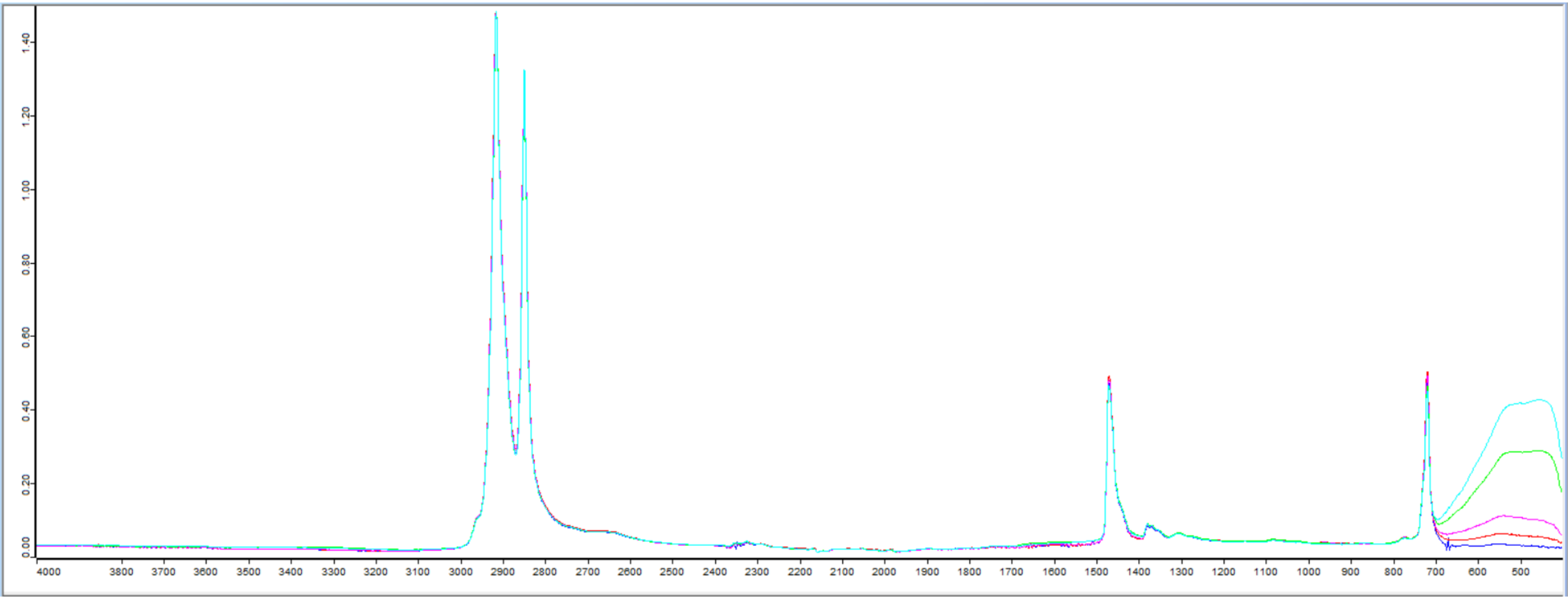
FTIR epoxy resin samples

- The absorbance between 400 cm^{-1} and 500 cm^{-1} wavenumbers increased
- MgO 30% at 3700 cm^{-1}



FTIR LLDPE samples

- LLDPE: absorbance increased around 500 cm^{-1}



Future Works

- Starting of ageing procedures — gamma irradiation
- Measurement of dielectric, mechanical parameter and FTIR parameters
- Identification of degradation mechanism
- Suggestion for non-destructive and on-site test method to track degradation